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Purgatorio calculations of Zbar at melt

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Disclaimer

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Purgatorio calculates self-consistent bound and continuum electron densities $\rho_{\text{bound}}(r)$ and $\rho_{\text{continuum}}(r)$ in a neutral ion sphere with radius R_{ion} by populating relativistic wave functions P(r) and Q(r) according to their statistical weights and the Fermi distribution function $f(\varepsilon,\mu) = (1+e^{(\varepsilon-\mu)/\tau})^{-1}$. The chemical potential μ is varied to ensure neutrality:

$$\int_0^{R_{\text{ion}}} 4\pi r^2 \rho_{\text{tot}}(r)\mathrm{d}r = Z$$

with

$$\rho_{\text{tot}}(r) = \rho_{\text{bound}}(r) + \rho_{\text{continuum}}(r)$$

$$4\pi r^2 \rho_{\text{bound}}(r) = \sum_i f(\varepsilon_i, \mu) 2|\kappa_i| \left\{P_i^2(r) + Q_i^2(r)\right\}$$

$$4\pi r^2 \rho_{\text{continuum}}(r) = \int_0^{\infty} \mathrm{d}\varepsilon\, f(\varepsilon, \mu) \sum_\kappa 2|\kappa| \left\{P_{\kappa,\varepsilon}^2(r) + Q_{\kappa,\varepsilon}^2(r)\right\}$$

While the free-electron density of states $X^{\text{ideal}}(\varepsilon) = p(1+\alpha^2\varepsilon)/(\pi^2 n)$ varies smoothly with the electron energy, the density of states obtained from the wave functions can include sharp features due to quasi-bound resonant states, continuum states with positive energies whose wave functions are fairly localized about the ion center. This quantity is:

$$X(\varepsilon) = \sum_\kappa 2|\kappa| \int_0^{\mathrm{R}_{\text{ion}}} \mathrm{d}r \left\{P_{\kappa,\varepsilon}^2(r) + Q_{\kappa,\varepsilon}^2(r)\right\}$$

The average ion charge can be computed in several ways. The most straightforward of these is to define the ion charge to be the total number of continuum electrons:

$$Z_{\text{continuum}} = Z_{\text{nuc}} - N_{\text{bound}} = \int_0^{R_{ion}} 4\pi r^2 \rho_{\text{continuum}}(r)\mathrm{d}r = \int_0^{\infty} f(\varepsilon, \mu) X(\varepsilon)\mathrm{d}\varepsilon$$

This definition includes both the electrons in the ideal density of states, which have wave functions distributed throughout the material, and the “quasi-bound” electrons in the resonance features. An alternative definition – the most reliable for transport calculations – counts only the free electrons in the ideal density of states, excluding resonances:

$$Z_{\text{background}} = \int_0^{\infty} f(\varepsilon, \mu) X^{\text{ideal}}(\varepsilon)\mathrm{d}\varepsilon$$

Finally, we can define the free electrons to be those on the surface of the ion sphere:

$$Z_{\text{WS}} = 4\pi R_{ion}{}^2 \rho_{\text{tot}}(R_{ion}) / n$$

This definition largely excludes electrons in continuum resonances but can include a portion of any negative-energy bound states that “leak out” of the ion sphere. The electrons on the surface of the ion sphere are free to move between ions and can thus be considered extensive.

Table of Z values at melt

Element	T_{melt}(eV)	ρ_{melt} (g/cc)	Z_{WS}	$Z_{background}$	$Z_{continuum}$
Al	0.0804	2.385	2.308	1.795	3.00
K	0.0290	0.77	1.078	1.021	1.00
Fe	0.156	7.05	2.335	1.527	8.00
Cu	0.117	7.96	1.955	1.352	11.00
Ag	0.106	9.45	2.019	1.333	11.00
Au	0.115	17.36	2.410	1.434	11.00
Pb	0.0518	10.2	1.797	1.107	2.224